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Low Cost, Efficient Microcavity Plasma Ozone Generation for Water Remediation and Air Purification

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14. ABSTRACT
EP PURIFICATION, INC. and the University of Illinois have formed a team to pursue the demonstration and commercialization of low cost, large arrays of microcavity plasmas capable of producing ozone efficiently. During this Phase I program experimental testing of several microplasma ozone generators in Phase I showed clearly that efficiencies much larger than those anticipated at the outset of the program are attainable. Efficiencies of 160 g/kWh were realized for O3 concentrations of tens of g/Nm3. The most promising results were measured with a stacked 36 microchannel array (parallel processing reactor for large scale ozone generation) for which efficiencies above 150 g/kWh were observed. The results of the Phase I program demonstrate that microplasma technology will match or surpass conventional corona discharge reactors in efficiency

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Air Force Phase I
Final Report:

Low Cost, Efficient Microcavity Plasma Ozone Generation for Water Remediation and Air Purification

Period of Performance:
9/1/2011 through 5/31/2012

Cyrus M. Herring, PI
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Contract Number: FA9550-11-C-0087

June 2012

TABLE OF CONTENTS

EDEN PARK ILLUMINATION
FINAL REPORT

I. **PROJECT SUMMARY**: EP PURIFICATION, INC. and the University of Illinois have formed a team to pursue the demonstration and commercialization of low cost, large arrays of microcavity plasmas capable of producing ozone efficiently. During this Phase I program we developed low cost ozone generators based on large arrays of microcavity plasmas. Modules capable of producing over 1.4g of O_3 per hour were fabricated and efficiencies of nearly 190mg/kWh at 3.3%wt concentration were realized. Phase II will be aimed at producing generators capable of generating several hundred grams per hour at an efficiency above that available with conventional technology.

II. **GOAL OF PROJECT**: The primary goal of this program was to demonstrate a new micro-reactor system for efficient water remediation or air purification. Arrays of microchannel devices having a cross-sectional dimension of less than a few hundred microns were fabricated to generate microplasmas in air and O_2 with active plasma reaction areas of 20 cm^2 (1" × 3") or more, that generated ozone at a rate of 1.4g/h. Improvements in ozone production efficiency were achieved by close packing of microplasma reactor units into a minimum volume to achieve a maximized reaction space and throughput.

III. ACHIEVEMENTS

A. Summary of Phase I Milestones

During the Phase I program, milestones were reached that are well beyond our expectations at the outset of this program. Specifically, the following levels of performance for a microplasma reactor were realized:

1. O_3 production efficiencies above 180 g/kWh were obtained at O_3 concentration levels in the reactor effluent beyond 3%wt. concentration using 12-channel devices. This efficiency is comparable to that for the best commercial reactors and is more than 8 times the expected output of the Phase I program.

2. The values cited in #1 above were obtained with a linear microplasma structure having 36mm long channels and a total reactor volume of ~0.032 cm^3. Estimates indicate that a full scale microplasma array reactor will have a weight and volume almost two orders of magnitude smaller than those for existing reactors.

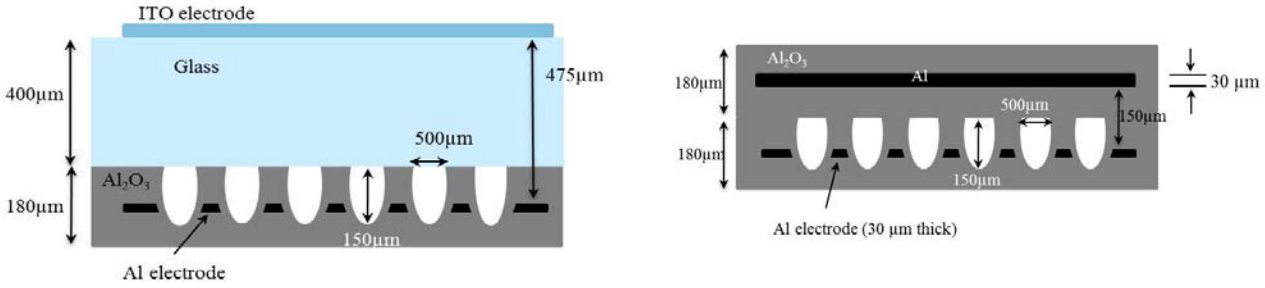
3. Ozone concentration of over 40 g/m^3 using 12 channel devices was accomplished at the oxygen flow rate of 0.1 L/min.

4. Preliminary research on long-term, continuous operation of the microplasma reactor shows more than 1600 hours of continuous operation without any performance degradation, and device operation for tens of thousands of hours will be one focus of the proposed Phase II program (years of continuous operation).

5. Al-Al electrode system shows superior performance in ozone production efficiency and concentration over glass dielectric based discharge system (which is being used in the conventional technology).

B. Detailed Description of Phase I Accomplishments

Our first task was to determine which structure, from a variety of options, is optimal from the perspective of efficiency and throughput. Two of the device structures that were examined are shown in cross-section in Figure 1. Both designs produce low temperature plasmas in microchannels ~ 2.2 cm in length (Figure 2) but the electrode and dielectric structures yield different results. Figure 3 summarizes the results of one comparison of the two designs of Figure 1. Specifically, the efficiency (expressed in units of g/kWh) for ozone production from pure oxygen feedstock is shown for both device types for a feedstock gas flow rate of 0.5 liters per minute. The Al/Al_2O_3 device structure is clearly superior to the Al/glass design. Efficiencies beyond 85 g/kWh are observed for O_3 concentrations of ~3 g/m^3.



(a) (b)

Figure 1. Two microplasma channel structures, representative of those examined in Phase I: a) an Al-glass device design, and b) a fully Al-Al_2O_3 design. In both cases, the reactor comprised 12 channels, each ~ 2.2 cm in length.

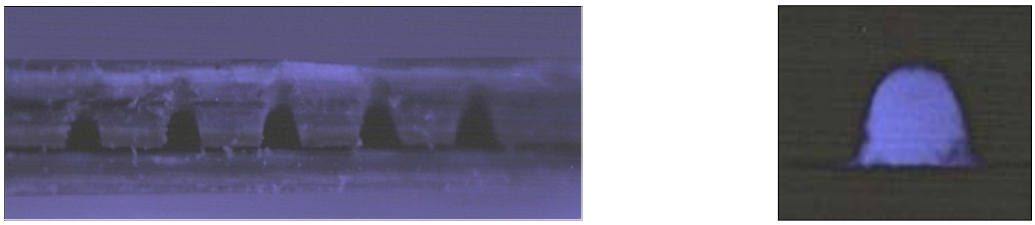


Figure 2. Cross-sectional optical microscope images of an array of microplasma channel devices fabricated in Al/Al_2O_3 structure (left) and uniform glow microplasma confined to the channel (right).

Once the general design of the microplasma channel cross-section was fixed, the operating parameters were varied. The dependence of ozone concentration on the electrical power dissipated by the reactor is presented in Figure 4 for two different values of the oxygen flow rate (0.5 L/min and 1.0 L/min). For these tests, the reactor comprised six microchannels each having a depth of 100 µm and a width of 125 µm. The feedstock gas is only in contact with nanoporous alumina lining a cavity produced by micro-powder blasting. Figure 4 shows that the concentration for ozone production is increased by prolonging the residence time of the oxygen in the microplasma channel. This can be accomplished by either reducing the mass flow rate or extending the length of the microplasma channels. In order to scale the mass throughput of our systems, we will resort to longer or multiple, sequential channels in future reactors.

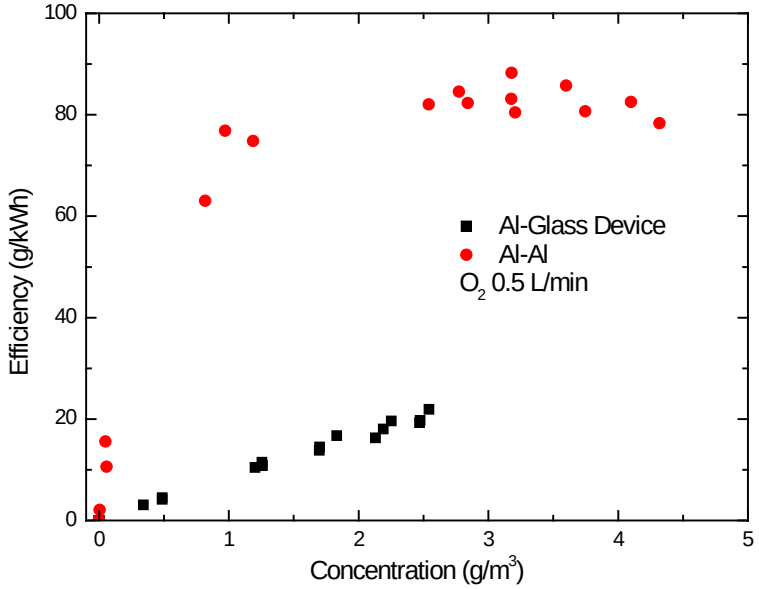


Figure 3. Comparison of the O_3 generation efficiency of an Al/glass structure with the performance of an Al/Al_2O_3 design of the same length. The flow rate for the O_2 feedstock gas was fixed at 0.5 L/min.

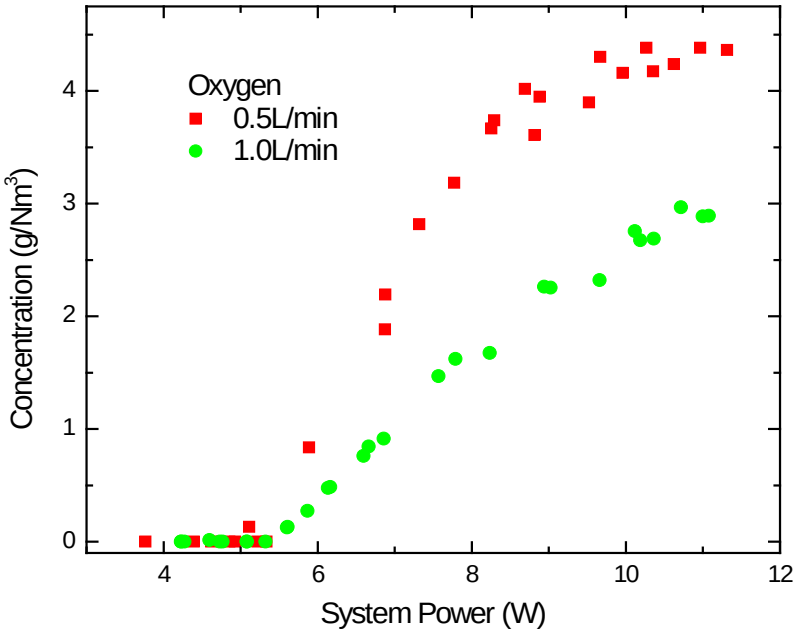


Figure 4. Variation of O_3 concentration (expressed in grams per normal m^3 (g/Nm^3)) with system power for two oxygen feedstock gas flow rates. One Nm^3 is a cubic meter of gas at standard temperature and pressure (STP).

When small amounts of nitrogen are added to the feedstock gas (1%), the performance of the reactor increases dramatically, as illustrated by the data of Figure 5. These results were obtained for a 12 channel reactor in which the channels had a width and depth of 200 µm and ~180 µm, respectively. Notice that the reactor efficiency has leapt to more than 160 g/kWh and maximum concentrations approaching 40 g/m^3 are obtained. It must be emphasized that the efficiencies of Figure 5 are more than a factor of 8 greater than the goal of 20 g/kWh that was set for the Phase I program. Addition of a small portion of nitrogen generates limited concentration of NO_x species which increases the ozone generation[1], and also reduces the operating voltage. Another encouraging aspect of these data is the fact that the efficiency holds approximately constant even though the O_2 feedstock flow rate is increased from 0.1 L/min to 0.5 L/min. This bodes well for further increases in both reactor efficiency and O_3 concentration in the effluent when the channel length is increased beyond 2.2 cm.

Preliminary parameterization studies of the microplasma reactors demonstrate that this technology will be readily scalable. As one example, consider the data of Figure 6 which show that the ozone concentration produced by a 12 channel reactor scales linearly with the power delivered to the array. Since concentration is inversely proportional to flow rate, higher concentrations are available by scaling the length and cross-sectional area of the channels.

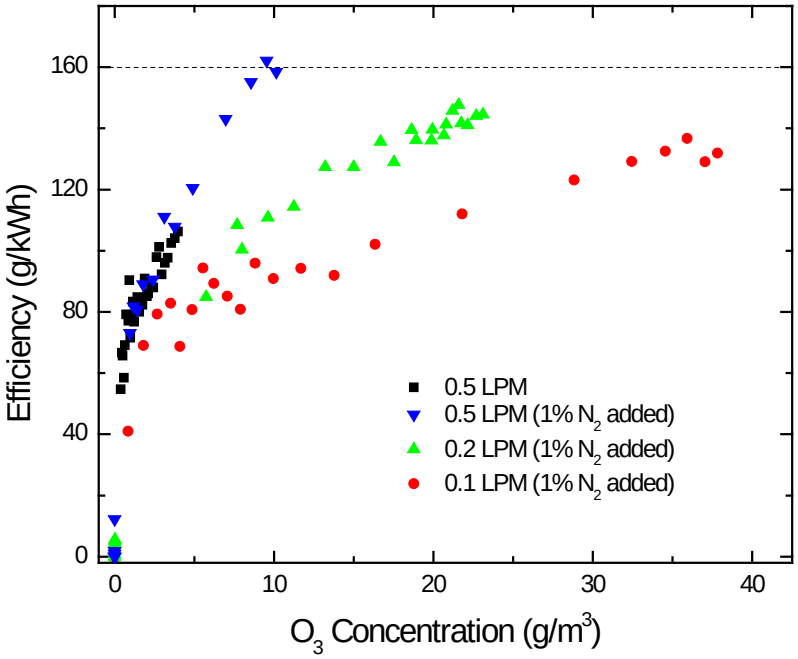


Figure 5. Variation of ozone concentration with reactor efficiency for a reactor comprising 12 microplasma channels fabricated in Al_2O_3 with channel widths and depths of 200 µm and 150 µm, respectively.

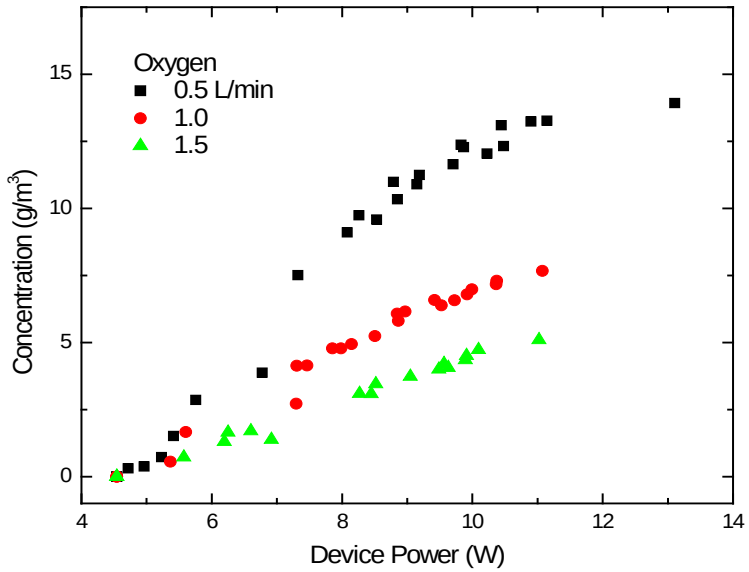


Figure 6. Dependence of the ozone concentration on the power dissipated by a 12 channel reactor. Data are given for three values of the oxygen flow rate.

A critical aspect of assessing the potential of microplasma technology for ozone generation is reactor lifetime, and Figure 7 presents data for device operation of >1600 hours. The device appeared stable during the lifetime testing. The device end of life was induced by operating under high concentrations of water vapor (10,000-20,000 ppm) after the 1600 hour point was reached. The regions in Figure 7 showing concentrations below 2.5% are when water vapor was added to the system. It was not until the 3rd test with water vapor that the device failed. These tests were conducted with a 12 channel Al/Al_2O_3 reactor producing O_3 at a concentration of 3 wt. % and an efficiency > 180 g/kWh. This reactor was run continuously for more than 1600 hours before failure occurred. During this entire test, the reactor was not cooled (intentionally, running at ~50C) and the microchannels were driven with fast, high voltage pulses in an effort to accelerate aging and identify failure mechanisms. Based on these and other lifetime data acquired in the past year, we estimate that the lifetime of a 200-300 microchannel module, defined as the time for 50% of the channels to fail is > 50,000 hours or ~ 6 years of continuous operation. Further extension in module lifetime will be gained through thickening the dielectric and tailoring the voltage waveform driving the generator. Because a key aspect of the reactor design will be the ease with which individual modules can be replaced without "bringing down" the reactor, module lifetimes of 6 years are expected to be more than acceptable.

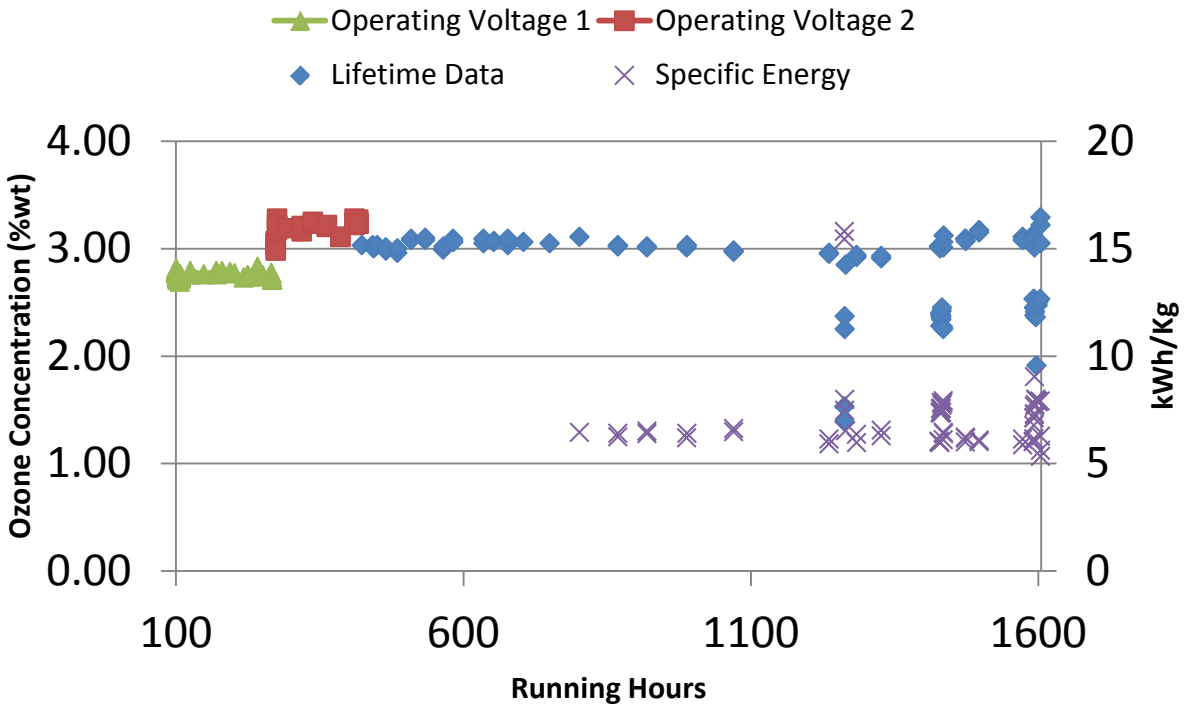


Figure 7. Ozone concentration vs. time. End of lifetime was brought about by running in high concentrations of water vapor (regions of relatively low concentration in figure).

One serious shortcoming of conventional corona discharge generators of O_3 is their sensitivity to water vapor. It is well-known that H_2O as an impurity in the oxygen or air feedstock gas produces nitric acid which quickly attacks metal surfaces and adversely

impacts system lifetime. For this reason, the maximum H_2O level specified for commercial reactors is < 5 ppm! Higher levels detected in the input gas will automatically shut down the system. Tests have been conducted to show microchannel plasmas to be robust with respect with water vapor. It took 20,000 ppm of H_2O (almost 4 orders of magnitude higher than the current limit for corona discharge reactors) to damage the reactor. Tests conducted show that the reactor efficiency returns to its full value when the H_2O concentration is lowered. Additional testing will be performed, but initial results show that the stringent requirements imposed by corona discharge systems for ultra-dry feedstock gas can be reduced with this new, microplasma technology, where only Al_2O_3 is exposed to the gas.

The culmination of the work conducted in the Phase I program is exhibited by the data of Figure 8. A composite reactor, fabricated by stacking six layers of 6 parallel microchannels, was tested for gas flow rates of 0.5, 1.0 and 1.5 L/min. Each of the 36 microchannels in the reactor had a width and depth of 500 µm and 200 µm, respectively. Efficiencies surpassing 150 g/kWh were measured for oxygen flow rates of 1.0 L/min and 1.5 L/min when the effluent O_3 concentration was between 5 and 20 g/Nm^3. It cannot be overemphasized that the efficiencies recorded in these experiments are more than 7 times greater than the value expected when submitting the Phase I proposal.

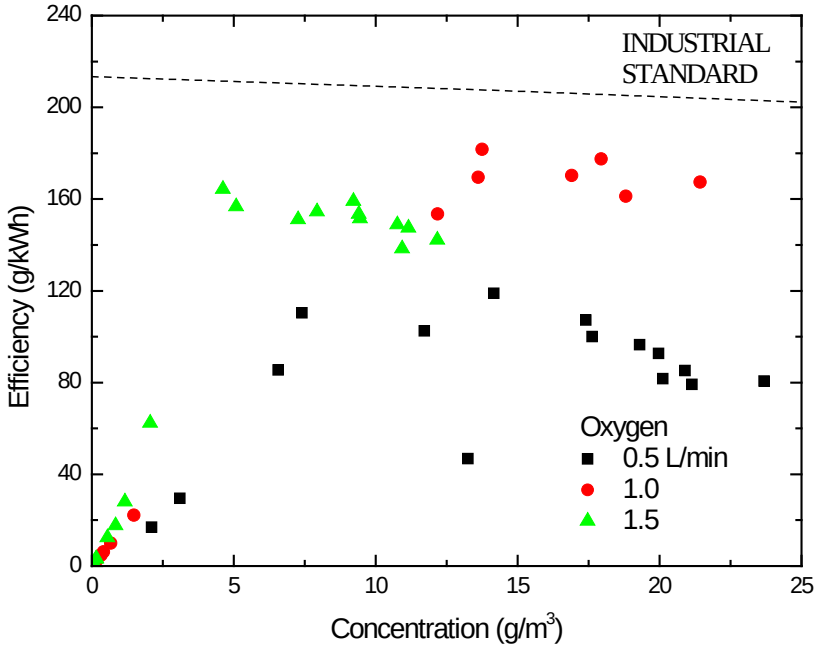


Figure 8. Dependence of reactor efficiency on O_3 concentration for a composite reactor fabricated by stacking six layers of 6 parallel microchannels with a channel depth of 200 µm and a width of 500 µm.

The horizontal dashed line in Figure 8 indicates a representative value for the efficiency that is offered by the best commercial ozone generators (very large-scale generators for municipality water treatment). Data collected for this proposal puts our best device operating at ~190g/kWh at 3.3%wt. concentration (43g/m^3, "off the scale" for the

above graph). The best commercial generators are at 192g/kWh at this concentration, and we believe with more optimization, we will surpass the efficiency that commercial generators can achieve.

In summary, experimental testing of several microplasma ozone generators in Phase I showed that efficiencies much larger than those anticipated at the outset of the program are attainable. Efficiencies of 190g/kWh were realized for O_3 concentrations of 40 g/Nm^3 with a production of ~230mg/h. The highest output results were measured with a 36 channel array for which efficiencies were above 150g/kWh at a production of 1.4g/h. The results of the Phase I program demonstrate that microplasma technology has the potential to match or surpass conventional corona discharge reactors in efficiency and they can tolerate higher concentrations of water vapor. Consequently, the Tasks proposed for a Phase II program will focus on the critical remaining issues: reactor lifetime, scaling of reactor throughput, and the size and weight of a full scale reactor (1 kg/h).

C. RESULTS

Devices were fabricated capable of >1600 hours of continuous operation with efficiencies nearly equal to that of the best commercial generators without signs of deterioration. Other devices were produced that could generate ~1.4g/h ozone. The devices consist of aluminum surrounded by Al_2O_3 oxide that appears to tolerate water vapor at higher concentrations than are allowed by conventional generators where metals are exposed to the resultant nitric acid formed from the water vapor. We believe this new family of ozone generators can work from efficient small scale ozone production to very large generators, with applications ranging from swimming pool treatment (minimizing the use of chlorine), to laundry treatment (eliminating the need for HOT water), to water treatment for city drinking water.

D. PROJECT STATUS AND PLAN

All the research and development cited above occurred as scheduled and the target goal details are listed above. Our efforts on the maximization of ozone concentration with continuous improvement of efficiency will be continued by optimization of the device geometry and electrical driving waveforms. Also, device reliability and lifetime with an extended operation will be investigated.

REFERENCES

1. U. Kogelschatz, B. Eliasson, and M. Hirth, “Ozone Generation from Oxygen and Air: Discharge Physics and Reaction Mechanisms,” *Ozone Sci. and Eng.*, vol. 10, pp. 367-378, 1998.

IV. RESEARCH PERSONNEL

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V. PUBLICATION

Some results obtained from this program are being temporally withheld from publication because of the sensitivity of the information with regard to commercializing this technology.